

What is claimed is:

1. A catalytic system for carbonylation which is;  
(A) a catalytic system comprising (A1) a Group  
VIII metal source of Periodic Table of the Elements,  
5 said metal source being supported on a carrier, (A2) a  
ligand and (A3) an acid, or

- (B) a catalytic system comprising (B1) a Group  
VIII metal source of Periodic Table of the Elements  
except for palladium, (B2) a ligand shown by the fol-  
10 lowing formula (Ib) and (B3) an electron donative com-  
pound having an electron donability  $\Delta vD$  relative to a  
deuterated methanol D of not less than 2:



- wherein A represents a phosphorus atom, an arsenic atom  
or an antimony atom; and  $R^1$ ,  $R^2$  and  $R^3$  independently  
represent a hydrogen atom, an optionally substituted  
alkyl group, an optionally substituted alkenyl group,  
20 an optionally substituted alkynyl group, an optionally  
substituted cycloalkyl group or an optionally substi-  
tuted aryl group, or  $R^2$  and  $R^3$  may together form an op-  
tionally substituted alkylene group, with a proviso  
that  $R^1$  to  $R^3$  are not concurrently hydrogen atoms.

- 25 2. A catalytic system for carbonylation as  
claimed in claim 1, wherein said Group VIII metal  
source (A1) in said catalytic system (A) is at least

one metal selected from the group consisting of cobalt, nickel, rhodium, palladium and platinum, or a compound of said metal.

3. A catalytic system for carbonylation as  
5 claimed in claim 1, wherein said carrier in said catalytic system (A) is at least one member selected from the group consisting of an activated carbon, a metal oxide, a nonmetal oxide and a clay mineral.

4. A catalytic system for carbonylation as  
10 claimed in claim 1, wherein said carrier in said catalytic system (A) has a specific surface area of 10 to 3,000 m<sup>2</sup>/g.

5. A catalytic system for carbonylation as  
15 claimed in claim 1, wherein the supporting amount of said Group VIII metal source (A1) in said catalytic system (A) is 0.01 to 20% by weight relative to the carrier.

6. A catalytic system for carbonylation as  
20 claimed in claim 1, wherein said ligand (A2) in said catalytic system (A) is at least one member selected from the group consisting of a phosphorus compound, an arsenic compound and an antimony compound.

7. A catalytic system for carbonylation as  
25 claimed in claim 1, wherein said ligand (A2) in said catalytic system (A) is a tertiary organic phosphine or a tertiary organic arsine.

8. A catalytic system for carbonylation as

76

claimed in claim 7, wherein said tertiary organic phosphine or tertiary organic arsine has an aryl group, a substituted aryl group or an aromatic heterocyclic group containing a nitrogen atom as a hetero atom.

5           9. A catalytic system for carbonylation as claimed in claim 1, wherein said Group VIII metal source (B1) in said catalytic system (B) is at least one metal selected from the group consisting of platinum, cobalt, nickel and rhodium, or a compound of said  
10 metal.

          10. A catalytic system for carbonylation as claimed in claim 1, wherein said catalytic system (B) comprises the ligand (B2) of the formula (Ib) where A is a phosphorus atom.

15           11. A catalytic system for carbonylation as claimed in claim 1, wherein said ligand (B2) in said catalytic system (B) is a compound of the formula (Ib) where at least one of  $R^1$  to  $R^3$  is an aryl group or a substituted aryl group.

20           12. A catalytic system for carbonylation as claimed in claim 1, wherein said ligand (B2) in said catalytic system (B) is a tertiary organic phosphine.

          13. A catalytic system for carbonylation as claimed in claim 1, wherein said electron donative  
25 compound (B3) in said catalytic system (B) is at least one member selected from the group consisting of an amine, an imine, an amide, an ether, a ketone, an

ester, a lactone, an aldehyde, a sulfoxide, a nitrile, a nitro compound, an aromatic hydrocarbon and an aliphatic hydrocarbon.

5 14. A catalytic system for carbonylation as claimed in claim 1, wherein said electron donative compound (B3) in said catalytic system (B) comprises at least one basic compound selected from the group consisting of an amine, an imine and an amide.

10 15. A catalytic system for carbonylation as claimed in claim 14, wherein said electron donative compound (B3) in said catalytic system (B) further comprises an ether or an ester.

15 16. A catalytic system for carbonylation as claimed in claim 1, wherein said electron donative compound (B3) in said catalytic system (B) is a secondary amine or a tertiary amine.

20 17. A catalytic system for carbonylation as claimed in claim 1, wherein said electron donative compound (B3) in said catalytic system (B) is a compound having an electron donability  $\Delta vD$  relative to a deuterated methanol D of 30 to 250.

25 18. A catalytic system for carbonylation as claimed in claim 1, wherein said catalytic system (B) comprises (B1) a platinum compound, (B2) a tertiary organic phosphine having at least one aryl group or substituted aryl group and (B3) an electron donative compound having an electron donability  $\Delta vD$  relative to

a deuterated methanol D of 50 to 250.

19. A catalytic system for carbonylation as claimed in claim 18, wherein said electron donative compound (B3) is a heterocyclic amine or an alkanola-  
5 mine.

20. A catalytic system for carbonylation as claimed in claim 1, wherein said catalytic system (B) further comprises (B4) an acid.

21. A catalytic system for carbonylation as  
10 claimed in claim 1 or 20, wherein said acid (A3) or (B4) is a proton acid or a Lewis acid.

22. A catalytic system for carbonylation as claimed in claim 21, wherein said proton acid is at least one member selected from the group consisting of  
15 an arylsulfonic acid, an alkylsulfonic acid, a carboxylic acid, a hydrohalogenic acid, sulfuric acid, nitric acid, a phosphoric acid and a perhalogenic acid.

23. A catalytic system for carbonylation which comprises;

20 (A) a combination of (A1) a palladium source, said palladium source being supported on a carrier having a specific surface area of 100 to 2,000 m<sup>2</sup>/g, (A2) a tertiary organic phosphine or a tertiary organic arsine and (A3) a proton acid, or

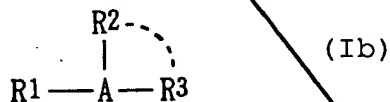
25 (B) a combination of (B1) a platinum compound, (B2) a tertiary organic phosphine, said organic phosphine having at least one aryl group or substituted

aryl group and being free from a nitrogen-containing heterocyclic group, (B3) an electron donative compound having an electron donability  $\Delta vD$  relative to a deuterated methanol D of not less than 2, and (B4) a proton acid.

24. A method for carbonylation which comprises allowing an acetylenic unsaturated compound or an olefinic unsaturated compound to react with carbon monoxide in the presence of;

(A) a catalytic system comprising (A1) a Group VIII metal source of Periodic Table of the Elements, said metal source being supported on a carrier, (A2) a ligand and (A3) an acid, or

(B) a catalytic system comprising (B1) a Group VIII metal source of Periodic Table of the Elements except for palladium, (B2) a ligand shown by the following formula (Ib) and (B3) an electron donative compound having an electron donability  $\Delta vD$  relative to a deuterated methanol D of not less than 2:



wherein A represents a phosphorus atom, an arsenic atom or an antimony atom; and  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  independently represent a hydrogen atom, an optionally substituted alkyl group, an optionally substituted alkenyl group, an optionally substituted alkynyl group, an optionally

substituted cycloalkyl group or an optionally substituted aryl group, or  $R^2$  and  $R^3$  may together form an optionally substituted alkylene group, with a proviso that  $R^1$  to  $R^3$  are not concurrently hydrogen atoms.

5        25. A method for carbonylation as claimed in claim 24, wherein said unsaturated compound is an  $\alpha$ -acetylenic compound or an  $\alpha$ -olefinic compound.

10        26. A method for carbonylation as claimed in claim 24, wherein said acetylenic unsaturated compound or olefinic unsaturated compound is allowed to react with carbon monoxide and a nucleophilic compound having a hydrogen atom which can be left in the reaction.

15        27. A method for carbonylation as claimed in claim 26, wherein said nucleophilic compound is at least one member selected from the group consisting of water, a compound having a hydroxyl group and a carboxylic acid.

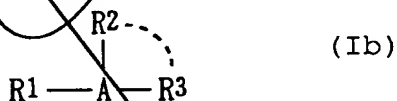
20        28. A method for carbonylation as claimed in claim 27, wherein said compound having a hydroxyl group is an alcohol.

25        29. A method which comprises allowing, in the presence of a catalytic system, (a) an asymmetric acetylenic or olefinic unsaturated compound to react with (b) carbon monoxide and (c) at least one compound selected from the group consisting of water, an alcohol having 1 to 20 carbon atoms and a carboxylic acid having 1 to 20 carbon atoms,

wherein said catalytic system is;

(A) a catalytic system for carbonylation comprising (A1) a Group VIII metal source of Periodic Table of the Elements, said metal source being supported on a carrier, (A2) a ligand and (A3) an acid, or

(B) a catalytic system for carbonylation comprising (B1) a Group VIII metal source of Periodic Table of the Elements except for palladium, (B2) a ligand shown by the following formula (Ib) and (B3) an electron donative compound having an electron donability  $\Delta vD$  relative to a deuterated methanol D of not less than 2:



wherein A represents a phosphorus atom, an arsenic atom or an antimony atom; and  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  independently represent a hydrogen atom, an optionally substituted alkyl group, an optionally substituted alkenyl group, an optionally substituted alkynyl group, an optionally substituted cycloalkyl group or an optionally substituted aryl group, or  $\text{R}^2$  and  $\text{R}^3$  may together form an optionally substituted alkylene group, with a proviso that  $\text{R}^1$  to  $\text{R}^3$  are not concurrently hydrogen atoms.

30. A method of producing an  $\alpha, \beta$ -ethylenic unsaturated carboxylic acid or a derivative thereof, which comprises allowing (a) an  $\alpha$ -acetylenic hydrocarbon to react with (b) carbon monoxide and (c) at least one nu-



cleophilic compound selected from the group consisting of water, an alcohol and a carboxylic acid, in the presence of;

5 (A) a catalytic system for carbonylation comprising a combination of (A1) a Group VIII metal source of Periodic Table of the Elements, said metal source being supported on a carrier, (A2) a tertiary organic phosphine or a tertiary organic arsine and (A3) a proton acid, or

10 (B) a catalytic system for carbonylation comprising a combination of (B1) a platinum compound, (B2) a tertiary organic phosphine having an aryl group or a substituted aryl group and being free from a heterocyclic group, (B3) a secondary amine or a tertiary amine,  
15 and (B4) a proton acid.

*add B1*